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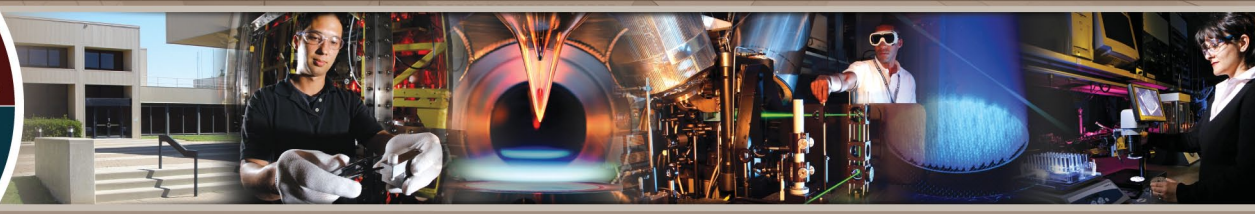

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An accurate vapor characterization protocol for measuring vapor pressures of volatile ingredients in composite explosives

Current terrorist strategies are focused on two principal goals: (1) mass casualties, such as attacks on airports, bridges, highways, and government buildings, and (2) remote attacks on military personnel and assets, such as transport vehicles and armored personnel carriers. These strategies are increasingly focused on the use of improvised explosive devices (IEDs). Early detection of these devices is critical to minimizing injury, loss of life, and damage to critical infrastructure or assets that can be caused by their use.

Currently, the best available systems are the dog/handler teams that have been in use since before World War I. Although canine-based "systems" have proven accurate and reliable over the last several decades, their shortfalls include a limited detection range, susceptibility to sensory fatigue and chemical overload, and the expense and time needed to replace the dogs if injured or killed.

Electronic systems that mimic the canine system and can overcome

(Continued on page 4)

Stratification effects in turbulent combustion

In direct-injection engines, fuel is injected directly into the combustion chamber to generate a highly stratified fuel–air mixture prior to ignition. This method can give more reliable ignition than alternative dilute, homogeneous combustion modes. The reduced fuel consumption, particularly at low-speed, light-load operation, is of great interest to both spark-ignition gasoline and compression-ignition diesel engine manufacturers.

While striving for improved fuel efficiency, designers must also satisfy increasingly restrictive emission criteria. Innovative engine designs that are needed to meet these combined requirements can be enhanced by both further insight and model validation for stratified combustion. In stratified combustion, the fuel and oxidizer are neither completely mixed nor completely segregated prior to combustion; thus, stratified combustion can not be adequately described by traditional modeling approaches, which are based on purely "premixed" or "nonpremixed" burning modes. Another example of stratified combustion is found in lean, partially premixed gas turbines used for power generation where locally richer mixtures are used to increase flame stability, while the globally lean flame produces extremely low NO_x emissions.

Present combustion devices have been highly optimized for the range of fossil fuels currently available. However, new fuels, such as hydrogen, synthetic, or biofuels, will require different conditions for effective and clean burning. Fuel stratification is being investigated as a core strategy for meeting the combined constraints of anticipated fuels,

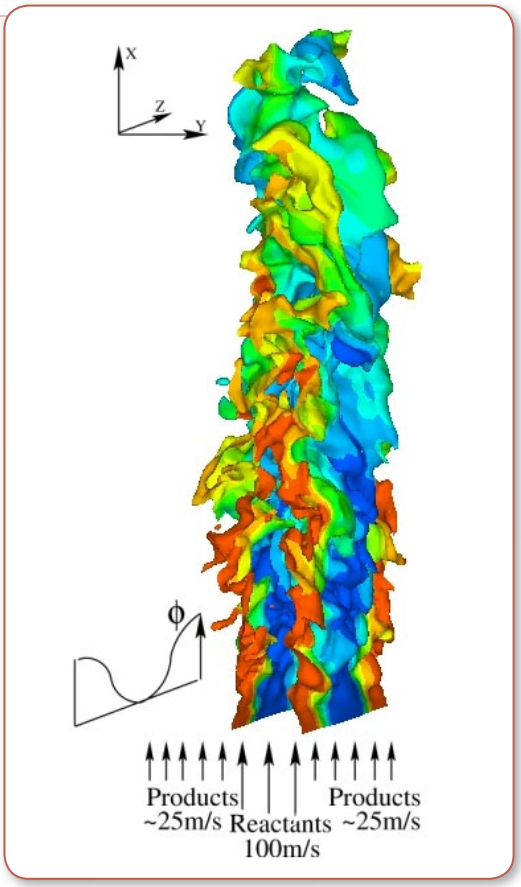

Figure 1. *A simulated stratified flame surface colored by equivalence ratio from blue at φ = 0.41 to red at φ = 1.0.*

pollutant emission, and fuel consumption, but models for stratified combustion modes still require considerable development and validation. Ed Richardson and Jackie Chen of the CRF's Reactive Flow department are engaged in a project producing fundamental simulation data for understanding stratified combustion. The benchmark simulation data resulting from this study will provide a unique test bed for predictive engineering models in the challenging partially premixed regime.

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Newsletter

Stratification effects in turbulent combustion (cont.)

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Modeling stratified flames

In 2008, the scope of the Turbulent Nonpremixed Flames (TNF) workshop was expanded to include stratified flames. The TNF is a framework for global collaboration on experimental measurement and model validation. Direct numerical simulation (DNS) will be an important component of this research, providing validation and insight for modeling the turbulence–chemistry interactions unique to stratified flames. The fully resolved, three-dimensional (3-D) turbulent flame simulations with detailed combustion chemistry are still limited by the capabilities of even the world's largest supercomputer to moderate Reynolds numbers. By selecting compact and computationally efficient DNS configurations, Richardson and Chen are able to complement one-dimensional (1-D) or planar experimental measurements of laboratory-scale stratified flames with complete descriptions of the interacting 3-D processes in model flames.

Figure 1 shows a simulated stratified flame surface colored by equivalence ratio (φ), which indicates the varying fuel–air concentrations. This configuration, which involves a turbulent slot Bunsen fuel jet issuing into a coflow of burnt products, enables intense turbulence to interact with the

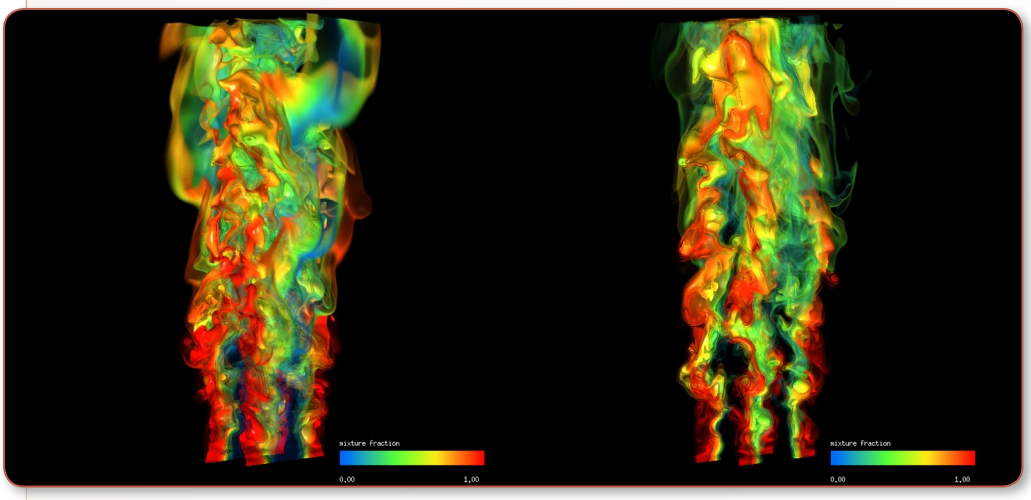

Figure 3. *Volume rendering of the heat release field colored by equivalence ratio for the low-stratification case (left: blue = 0.41, red = 1.0), and the high-stratification case (right: blue = 0.0, red = 1.4).*

flame front while preventing the flame from blowing out. Stratification is achieved by varying the equivalence ratio along the span-wise (z) direction. The stratification levels studied are centered about the perfectly premixed φ = 0.7 case investigated by Sankaran et al.,[1] extending via a low-stratification case $0.4 < \varphi < 1.0$, to a highly stratified case with equivalence ratio ranging from 0 (pure air) to 1.4.

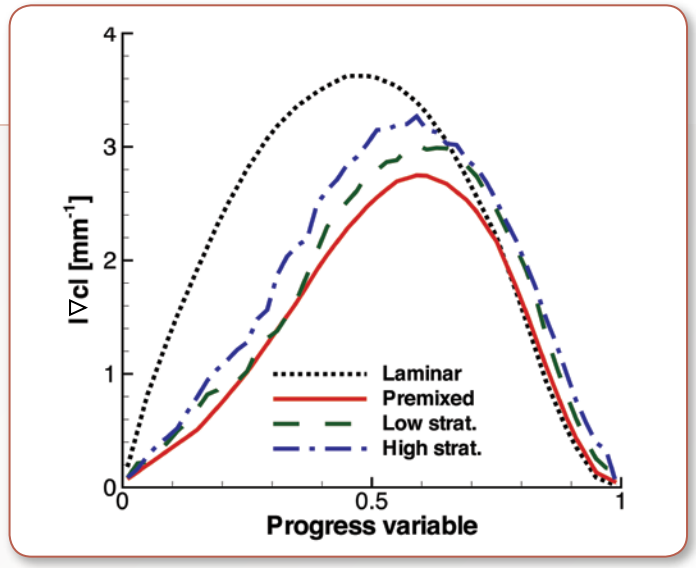

Figure 2. *The conditionally averaged flame normal progress variable gradient $|\nabla c|$ for a mixture with φ = 0.7 in the premixed, low-stratification, and high-stratification cases, as well as for unstrained laminar premixed flame propagation. Data are plotted at half of the jet flame length.*

Highly efficient, reduced methane–air chemical kinetic models have been optimized and validated for the simulation conditions by Tianfeng Lu at the University of Connecticut and Chung K. Law of Princeton University. These models include 13 or 19 transported species; the 19-species mechanism is being used to model rich flames, including their production of nitrogen oxides.

The jet slot width of 1.8 mm and a mean jet velocity of 100 m/s result in a jet Reynolds number of 2,100. The flame is highly wrinkled with significant flame–flame interactions.[1] Under these conditions, the flame is characterized by the thin reaction zones regime in which turbulent eddies penetrate the flame's preheat layer but are too large to disrupt the reaction zone.

The result is a thickened preheat layer identified by a reduction in the conditionally averaged progress variable gradient when compared to the laminar flame gradient. This process can be seen in Figure 2 for a mixture at φ = 0.7.

Volume rendering of scalar fields

The researchers have engaged two computer scientists, Hongfeng Yu at the CRF and Kwan-Lui Ma at the Institute of Ultrascale Visualization, which is part of the U.S. Department of Energy's Scientific Discovery through Advanced Computing (SciDAC) program, to perform a volume rendering of the scalar fields for improved insight. Figure 3 presents a volume rendering of the stratified flames' heat

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Jacqueline Chen receives 2009 Asian American Engineer of the Year award

The Chinese Institute of Engineers, USA has named CRF technical staff member Jacqueline Chen a recipient of the 2009 Asian American Engineer of the Year (AAEOY) award. The AAEOY, the only program of its kind, recognizes outstanding Asian American scientists and engineers for their significant contributions to their industries.

Photo by Randy Wong

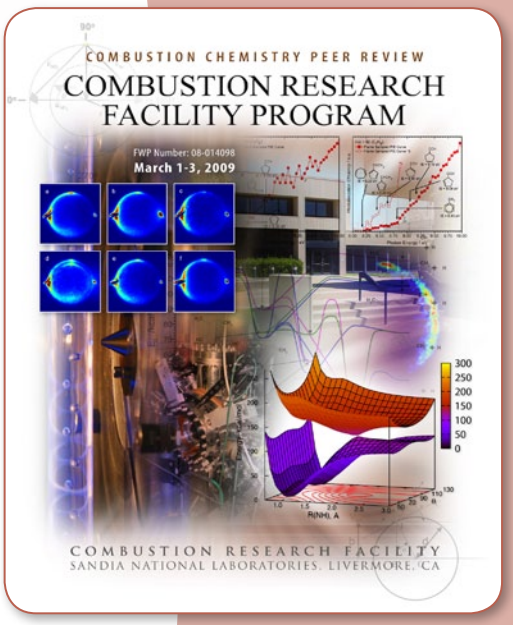
Chen has pioneered the use of petascale direct numerical simulations (DNSs) for turbulent combustion, with a focus on turbulence-chemistry interactions in canonical laboratory-scale flames. These simulations provide physical insight into the underlying science required to develop predictive models for designing clean and fuel-efficient internal combustion engines (ICEs) that can use 21st-century alternative fuels.

"Jackie has demonstrated the scientific excellence and leadership that most scientists aspire to," says Wen Hsu, manager of the CRF's Remote Sensing and Energetic Materials department. "She had the foresight to recognize many years ago that the capabilities of supercomputers would grow so rapidly that computationally intensive direct numerical simulations of complicated processes would soon become a viable approach to model combustion processes at realistic spatial and temporal scales. Her achievements have been recognized by many DOE Office of Science awards over the past several years."

Chen's current project, "High-Fidelity Simulations for Clean and Efficient Combustion of Alternative Fuels," is a partnership with Sandian Joe Oefelein and Oak Ridge National Laboratory. The project seeks to perform high-fidelity simulations of the complex aero-thermo-chemical interactions typically encountered in ICEs with an emphasis on fuel variability.

CRF hosts the CRF Combustion Chemistry 2009 peer review

On March 1-3, Mark Linne of the CRF hosted the Office of Basic Energy Sciences (BES) Combustion Chemistry Peer Review. This review provides BES program managers with independent technical evaluations of the scientific and/or technical merit of their projects, evaluates the appropriateness of the program's proposed methods or approaches; and verifies the competency of personnel and reasonableness of resources and budget. All research projects supported by BES undergo regular peer review every few years; this review was an opportunity to showcase the CRF's Combustion Chemistry programs, accomplishments, and ongoing work, as well as discuss possible directions for future research.



Topics presented over the two-day review included

- *Elementary Reaction Kinetics of Combustion Species (Craig Taatjes)*
- *Spectroscopy and Chemical Mechanisms (David Osborn)*
- *Theoretical Chemical Kinetics (Ahren Jasper)*
- *Flame Chemistry and Diagnostics (Nils Hansen)*
- *Chemical Dynamics for Ultra-Cold Molecules (David Chandler and Kevin Strecker), and*
- *Chemical Kinetics and Combustion Modeling (Jim Miller)*

Signatures and vapor pressures (cont.)

(Continued from page 1)

the inherent limitations of a dog/handler team are currently under development. In collaboration with Lawrence Livermore National Laboratory (LLNL) under the DOE/NNSA office of Nuclear Counter-Terrorism (NCT), CRF researchers Sean Maharrey, Aaron Highley, Deneille Wiese-Smith, and Richard Behrens are investigating one possible strategy for early detection/mitigation of explosives: standoff detection of the vapor-phase chemical signatures of the high explosives contained within the IED.

The CRF team recently published the results of an investigation of simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) measurements of vapors that evolve from several common explosive formulations (SAND2008-7013). The team measured the vapor pressures of the main ingredients and any identifiable minor species found in five different explosive formulations commonly used in current IEDs.

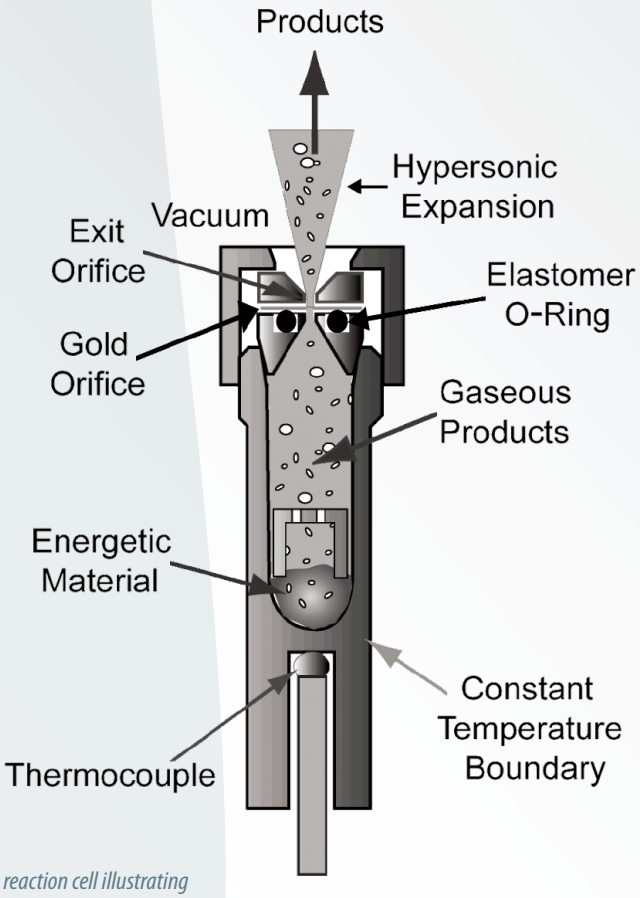


Figure 1. *Cross section of a reaction cell illustrating the sample configuration used in an STMBMS experiment. As the vapor flows through the orifice, each constituent is identified, and its rate of flow through the orifice is determined.*

To develop standoff explosive detectors, it is necessary to know what chemical species are available for detection. Generally, the energetic solids (i.e., RDX, PETN, HMX), which typically compose >85-90% of the explosive formulation, are so low in volatility that they provide almost no vapor to detect; nonetheless, explosives based on these compounds can be detected by some schemes, including detector dog/handler teams. This fact suggests that the chemical signatures being detected are not the parent chemical explosive molecule, but rather some combination of the more volatile minor ingredients in the explosive.

Typical techniques used to measure the vapor pressures of a compound are only able to obtain accurate measurements for pristine, highly purified compounds. Similarly, techniques that measure the distribution of species evolving from a compound at a given temperature (i.e., thermal desorption gas-chromatography/mass spectrometry) do not provide a means to accurately determine the corresponding thermogravimetric analysis (TGA) data so that the data can be accurately quantified. Because of these confounding factors, current techniques cannot accurately or reliably provide vapor pressure or sublimation rate measurements for a complex, multiconstituent explosive formulation.

The STMBMS instrument provides a unique combination of the features of differential-TGA instruments and rapid-scanning mass spectrometry instruments, along with precision molecular beam techniques, to enable accurate and reliable measurements of the vapor pressures and sublimation/evaporation rates of all species that evolve from a material over a given temperature range. The details of the STMBMS instrument and corresponding analysis methods have been described previously.

The basic features of a thermal desorption experiment using the STMBMS instrument are illustrated in Figure 1. A small sample of an explosive formulation is placed in an alumina reaction cell, which is sealed with a cap assembly containing a disk of gold foil. In the center of the disk is a hole with a specific diameter. The reaction cell is heated, using the thermocouple to measure and control the temperature of the cell. As the reaction cell is heated, vapor from the sample—and any other compounds within the cell—fills the free volume. As the vapor flows through the orifice, each constituent is identified, and its rate of flow through the orifice is determined. The measurements provide the time-dependent rate of formation of each gaseous species that is present solely in the gas phase within the reaction cell. The measurements also provide the vapor pressure of gaseous species that are in quasi-equilibrium with material in condensed phases.

(Continued on page 5)

Signatures and vapor pressures (cont.)

(Continued from page 4)

The pressure of gases within the reaction cell is determined by the diameter of the orifice and the experimental conditions. The gas pressure within the cell is determined by a steady-state balance between the rate of gas formation from the sample and the rate of exhaust through the orifice. For compounds in a two-phase quasi-equilibrium the pressure is determined by the temperature of the reaction cell and the properties of the compounds. In this case, a smaller orifice results in less of the gas exiting the reaction cell.

The vapor pressures of each ingredient in a formulation can be measured by recording the identities and rates of formation of the different vapors that flow through the orifice and out of the reaction cell over a range of experimental conditions. The vapor conditions are controlled by using a series of low-temperature isothermal steps to determine the temperature dependence of each ingredient's vapor pressure, and by cycling the isotherms to look for indications of ingredient interactions within the formulation.

Figures 2 through 4 display the results of a vapor pressure analysis for a 2004 manufactured lot of composition C4 explosive. Figure 2 contains a weight loss vs. temperature plot, indicating the temperature at which each ingredient evolves. Figure 3 shows a gas evolution rate vs. temperature plot for those ingredients, which demonstrates how quickly each ingredient evolves at a given temperature. Finally, Figure 4 plots the vapor pressure calculated for each heating and cooling cycle for each of the measured ingredients. Changes in the calculated vapor pressures of an individual ingredient during the different cycles can indicate interactions between ingredients that affect the volatility of each ingredient.

The results from this lot of C4 indicate that the di-methyl, di-nitro-butane (DMNB) taggant used in this formulation has a constant vapor pressure throughout its lifetime that is not affected by any of the other ingredients. For the RDX and Sebacate ingredients, however, the two different Sebacate curves in Figures 2 and 3 indicate an initial interaction of the Sebacate with the RDX. This interaction shows that ~30% of the Sebacate has adsorbed onto the surface of the RDX particles and evolves with a significantly higher vapor pressure than for the pristine Sebacate.

After this initial Sebacate loss, the vapor pressure drops to that of pristine Sebacate, indicating that this is effectively "free" Sebacate in the system. Results indicate that for a composition C4 formulation, the DMNB taggant and the adsorbed Sebacate have a well-defined chemical signature that can be used to identify C4, while the "free" Sebacate vapor pressure is much too low to be an effective signature. Since the evolution rate of Sebacate is minimal at low temperatures, it is expected that the 30% adsorbed Sebacate component will form a viable signature for a significant portion of the C4's nominal lifecycle. Results similar to the above have been developed for Sem Tex-1H, Composition B, Composition B3, and Red Dot.

The CRF team's investigation shows that the most likely form of any explosive gas-phase vapor fingerprint will not include the solid energetic (RDX and PETN) ingredients of the formulations. The solids tend to exhibit vapor pressures at low temperatures (<40°C) below the current ppt detection limits of most currently available chemical sensors. However, an accurate vapor fingerprint for an explosive can be obtained from the various plasticizers, stabilizers, and added taggants. These compounds tend to have vapor pressures at low temperatures that are well above the detection limits of currently available sensors.

A follow-up report currently underway will use the results of this study in combination with an LLNL detection study to develop an accurate and reliable vapor fingerprint for each of the formulations studied. This report will define the required detection sensitivities and chemical selectivities needed by a detection platform designed for these and similar explosive formulations.

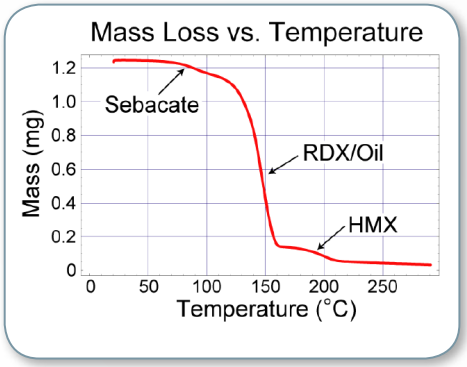


Figure 2. *Typical mass loss profile for a composition C4 mass spectrometry experiment. The plot shows the relative mass loss and corresponding temperature of evolution of several of the main ingredients used in a C4 formulation.*

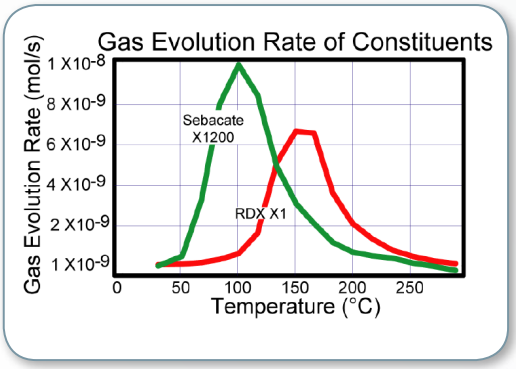


Figure 3. *Quantified gas evolution rates of some C4 constituents. The different gaseous species evolve from a sample as it is heated.*

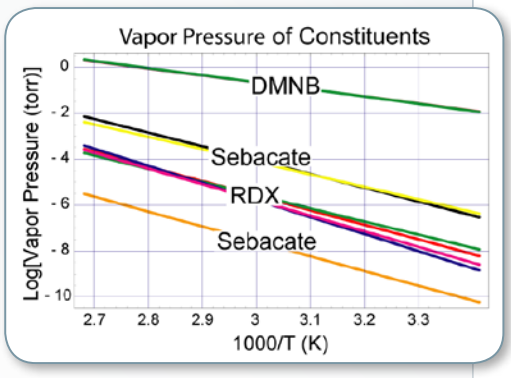


Figure 4. *Vapor pressure plot for various C4 ingredients. Variations in the calculated vapor pressure of an ingredient during the different heating and cooling cycles can give an indication of interactions between the individual ingredients that affect the volatility of each ingredient.*

Stratification effects in turbulent combustion (cont.)

(Continued from page 2)

release fields, again colored by equivalence ratio. As the equivalence ratio falls to φ = 0.4 and subsequently drops below the lean flammability limit, a dramatic reduction occurs in the heat release rate. The areas of weakly burning flame are more susceptible to disruption by the turbulent motions, permitting study of the broken reaction zones' combustion regime.

Equivalence ratio gradients

As the initial fuel–air stratification dissipates due to turbulent mixing, the flames are subjected to steep, time-varying equivalence ratio gradients. Locations where the equivalence ratio gradients align normal to the flame exhibit greatly modified burning rates and flame propagation speeds, S_d, compared to the perfectly premixed case. Figure 4 shows the variation of propagation speed with the flame-normal equivalence ratio gradient, indicating enhanced flame speeds when the products are richer than the reactants, as well as the reverse. The figure's symbols are colored by the strain rate normal to the flame because the magnitude of the equivalence ratio gradient, but not its orientation, is strongly correlated with the local fluid dynamic strain.

A study of this effect using computations of strained 1-D counterflow flames in the presence of equivalence ratio gradients[2] reveals the thermo-chemical basis for this observation. Specifically, equivalence ratio gradients resulting in flames with richer, higher-temperature products lead to enhanced equilibrium concentrations of species such as the hydroxyl radical in the flame's carbon monoxide–hydrogen

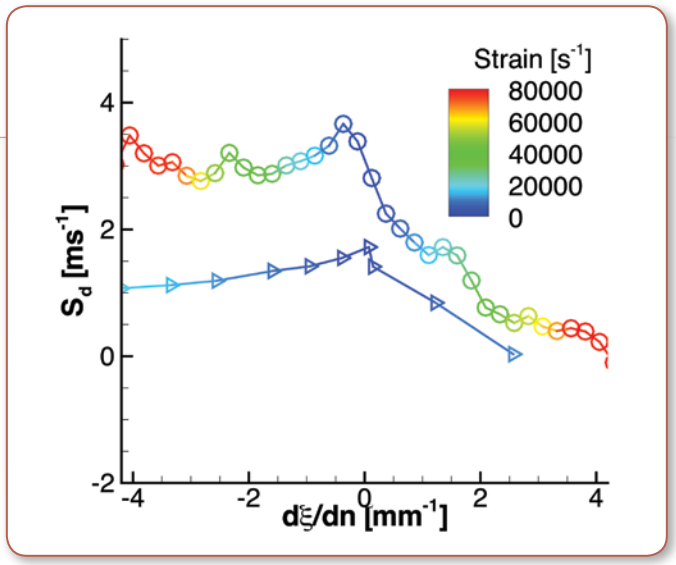


Figure 4. *The variation of flame propagation speed, S_d, with the flame normal equivalence ratio gradient. Data are conditionally averaged on the 1,400-K iso-surface and φ = 0.7 in the low-stratification case (circles). Symbols are colored by the flame normal strain rate. Data for 1-D counterflow computations are plotted with triangular symbols.*

recombination layer. The diffusion of these highly reactive intermediate species towards the reactant side of the flame, as opposed to thermal diffusion, is the main source of the increased reaction rate. Data from the 1-D simulations are included in Figure 4. The similarity between the trends in the 1-D and DNS data establishes the stratified counterflow configuration as a valid paradigm for understanding and modeling turbulent combustion with fuel–air stratification.

[1] R. Sankaran, J.H. Chen et al., "Structure of a spatially developing turbulent lean methane–air Bunsen flame," *Proc. Combust. Inst. 2007*, **31**, 1291–1298.

[2] E.S. Richardson, J.H. Chen et al., "Effects of equivalence ratio variation on lean, stratified methane–air laminar counterflow flames," 6th Mediterranean Combustion Symposium, Ajaccio, France, 2009.

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